Indian J. Phys. **75A** (4), 343-345 (2001)

IJP A
— an international journal

The role of praseodymium in $Y_1Ba_2Cu_3O_7$ high temperature superconducting compounds

B N Dole, R R Kothawale and S S Shah*

Department of Physics, Dr B A Marathwada University, Aurangabad-431 004, Maharashtra, India

E-mail . sss phy@mailexcite.com

Abstract : Praseodymium is playing very interesting role in $Y_1Ba_2Cu_3O_7$ high T_c superconducting compounds when yttrium is partly replaced by praseodymium. Superconductivity is suppressed as Pr content is increased, there is no unique agreement in experimental results about the role of Pr in these compounds. XRD and Neutron Diffraction work is done on these compounds when yttrium is replaced upto 50% by Pr. Samples were prepared by solid state reaction method and chemical route. The XRD and ND results on lattice parameters, orthorhombocity are reported in those samples and the observed differences in these results are discussed. The possible existence of Pr in 3+ and 4+ valence states is discussed on the basis of XRD, lattice parameter variations and orthorhombocity. The results indicate that the presence of praseodymium is in 3+ state Decreasing in puckering and increase in Cu(1) - O(4) bonds is responsible for suppression of T_c

Keywords · Superconducting compounds, orthorhombicity, lattice parameters

PACS No. 74.72.Bk

1. Introduction

It is well known that substitution of Pr in $YBa_2Cu_3O_{7-\delta}$ high T_c superconducting compounds suppresses the superconductivity while other rare earth compounds affect superconductivity while other rare earth compounds affect superconductivity insignificantly. The absence of superconductivity in above compounds has attracted a lot of attention of researchers. The Hall effect, magnetic susceptibility and chemical substitution studies support the substitution of Pr in 4+ valence state is responsible for the suppression of T_c. However, crystal field theories, band studies and X-ray studies give support to Pr substitution consistent with Pr^{3+} for Yttrium. The variation of T_c with Pr substitution was explained by magnetic pair breaking theory and hole localisation are simultaneously responsible for T_c suppression in these compounds. We have characterised these samples by X- ray diffraction and Neutron diffraction and tried to understand the problem.

2. Experimental details

The samples $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ with compositions $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5 were prepared by solid state reaction route and chemical route [1-5]. The solid state reaction route is well known and usually employed for the preparation of the superconducting samples. Here, the other and important route is used for the processing of the samples known as chemical route. For the sintering purpose of the samples, we have used programmed carbolite furnace. The appropriate mixtures of high purity (Aldrich made 99.99%) Y_2O_3, $BaCO_3$, Pr_6O_{11} and CuO were used. The powders were mixed, ground and calcined at

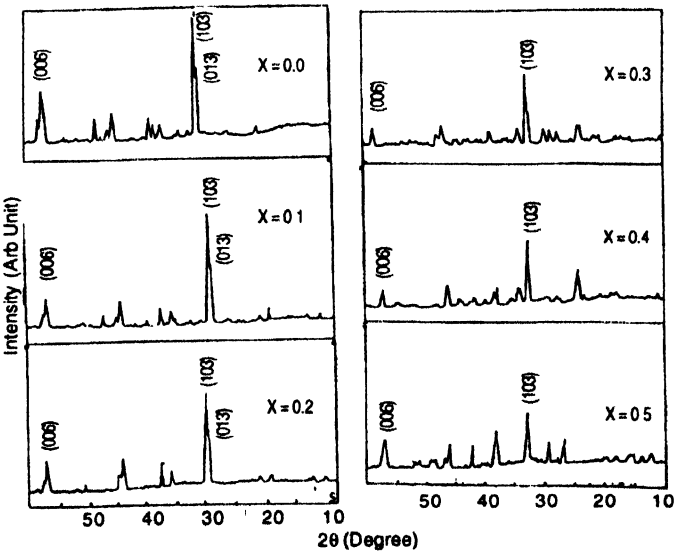

Figure 1. X-ray diffraction patterns of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ samples, prepared by solid state reaction route.

* Corresponding Author

910°C for 24 h in air, secondly calcined at 920°C for 24h and sintered at 930°C for 24 h with intermediate grindings. The samples were pressed into pellets. These pellets were annealed in oxygen atmosphere for 24 h at 920°C followed by slow cooling at 1°C/min. to 450°C where they remained for 16h before a final cooling to room temperature at 1°C/min.

3. Results and conclusion

The X-ray diffraction patterns of the system $Y_{1-x}Pr_xBa_2Cu_3O_{7-d}$ with $x = 0.0, 0.1, 0.2, 0.3, 0.4$ and 0.5 were taken as shown in Figure 1 which is prepared by solid state reaction method and chemical route as shown in Figure 2. The X-ray patterns show

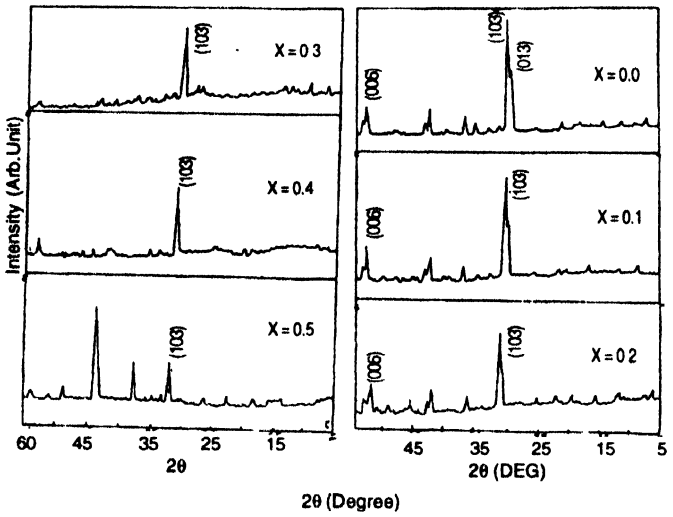

Figure 2. X-ray diffraction patterns of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ samples, prepared by chemical route.

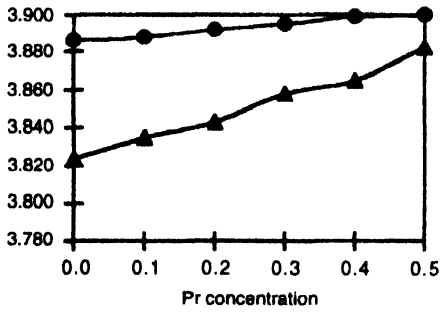

Figure 3(a). Samples prepared by solid state reaction method and data is taken from XRD. Lattice parameter *a* is increasing while *b* is nearly constant.

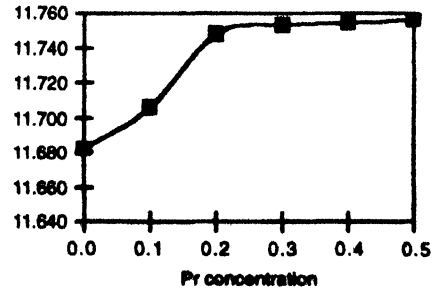

Figure 3(b). Pr concentration *vs* lattice parameter *c* of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ samples.

that the samples are well prepared as shown in Figures 3(a, b), prepared by solid state reaction route. The variation of lattice parameters *a*, *b* and *c* with praseodymium concentration indicates that *a* increases rapidly as compared to *b*. The values of lattice parameters *a*, *b* and *c* are close to values reported in literature [6]. There is considerable variation of *a* as compared to *b* and *c* which increases with praseodymium and orthorhombicity goes on decreasing as listed in Table 1 and shown in Figure 4 with

Table 1. Lattice parameters, volume cell and orthorhombicity of samples with corresponding Pr content.

Pr Conc	Lattice Parameters (Å) a	b	c	Volume Cell (Å)³	Orthorhombicity (b-a)/(a+b)
0.0	3.824	3.886	11.682	173.595	0.00804
0.1	3.835	3.888	11.706	174.542	0.00686
0.2	3.843	3.892	11.748	174.714	0.00633
0.3	3.858	3.895	11.753	175.998	0.00594
0.4	3.865	3.899	11.754	177.144	0.00437
0.5	3.882	3.900	11.756	177.986	0.00231

praseodymium. Comparing the ionic radii [7] of Pr^{3+} and Pr^{4+} with Y^{3+}, one can conclude that praseodymium goes to Y site in Pr^{3+} state rather than in Pr^{4+} state up to $x = 50\%$. If praseodymium is in Pr^{4+} state, the variation of *a*, *b* and *c* should show decreasing

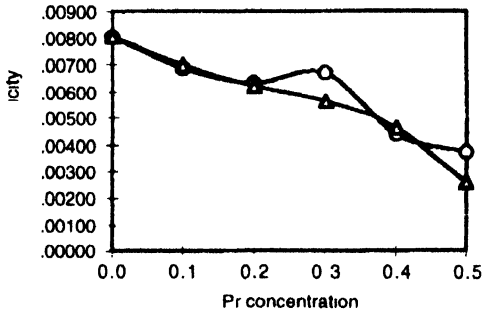

Figure 4. Pr concentration *vs* orthorhombicity of $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ samples.

trend or decrease at least after $x = 0.5$ where superconductivity is totally lost for $x = 0.55$ [8]. Results of neutron diffraction show that samples are well prepared with correct oxygen content with very little impurity phases. Praseodymium content is almost exact. From the bond lengths (Table 2) and particularly from Ba-

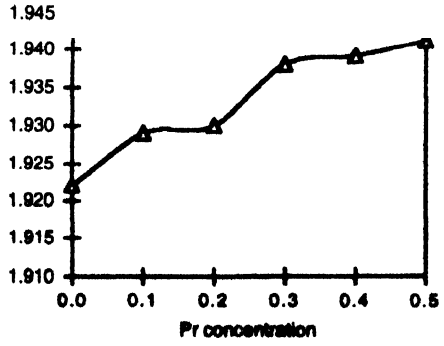

Figure 5. Pr concentration *vs* Ba-O(2) distances.

Table 2. Bond distances in Å (estimated from X-ray studies)

Bond	Pr content					
	0 0	0 1	0 2	0.3	0 4	0.5
Ba – O(1) *2	2.853(3)	2.855(3)	2.849(3)	2.863(3)	2 848(3)	2.857(3)
Ba – O(2) *4	2.730(1)	2.740(1)	2.741(1)	2 749(1)	2 746(1)	2 753(1)
Ba – O(3) *2	3.034(9)	3 060(9)	3.019(6)	3 060(9)	3.032(9)	3.040(9)
Ba – O(4) *2	2.960(9)	2 970(9)	2.971(7)	2 941(9)	2 949(9)	2 960(9)
Y – O(3) *4	2.376(7)	2.370(7)	2.407(4)	2 381(7)	2 404(6)	2.403(7)
Y – O(4) *4	2.393(8)	2 403(7)	2 406(5)	2.439(7)	2 435(6)	2.436(6)

O(2) distances, it is clear that puckering goes on decreasing as bond length Ba-O(2) goes on increasing as shown in Figure 5. The suppression of T_c is related with the decrease in puckering. The distance of centre of puckered plane is square root of $\{[(Ba\text{-}O(2)]^2 - (b/2)^2\}$ away from the yttrium. The neutron diffraction data of our samples is taken from DHRUVA reactor, Mumbai. Also from Neutron diffraction, we see the increasing trend in Y-

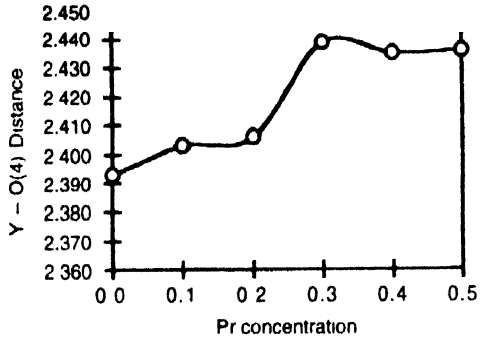

Figure 6. Pr concentration *vs* Y-O(4) distances.

O(4) distances as shown in Figure (6) which is consistent with the variation of *c*. One can conclude that as the distance Cu(1) – O(4) goes on increasing, electron- phonon interaction decreases [9]. This is the cause of suppression in superconductivity. From the XRD data, one can conclude that upto $x = 0.5$, praseodymium goes to Y site in Pr^{3+} form. Also decreasing in puckering and increase in Cu(1) - O(4) bonds is responsible for suppression of T_c. The results indicate that the presence of praseodymium is in 3+ state. It is necessary to work for samples with $x = 0.6$ to 1.0.

Acknowledgment

We are thankful to IUC-DAEF, Indore for giving the financial assistance to this work.

References

[1] B Rupp, E Porschke, P Meuffels, P Fischer and P Allenspach *Phys Rev* **B40** 4472 (1989)

[2] J D Jorgenson, B W Veal, W K Kwok, G W Carbtree, A Umezawa, L J Mowicki and A P Paulikas *Physical Rev* **B36** 5731 (1987)

[3] K Kishio, J Shimoyama, T Hasegawa, K Kitzawa and K Fueki *Jpn J Appl Phys* **26** L 1228 (1987)

[4] A Ono and Y Ishizawa *Jpn J Appl Phys* **26** L 1043 (1987)

[5] L M Schneemeyer, J V Waszczak, T Siegrest, R B Van Dovr, L W Rupp, B Batlogg, R J Cava and D W Murphy *Nature* **328** 601 (1987)

[6] J L Peng, P Klavins, R N Shelton, H B Radousky, P A Hahn and L Bernardez *Phys Rev* **B40** 4517 (1989)

[7] R D Shannon *Acta Cryst.* **B26** 1076 (1970)

[8] H Srikanth, S Sridhar, D A Gajewski, M B Maple *Physica* **C291** 235 (1997)

[9] M Andersson, O Rapp and Tellgren *Physica* **C205** 105-110 (1993)